

Hydrogenation of German bituminous coal for distillates
by I. Romey, F. Friedrich, B. Strobel

More than fifty years ago already, conversion of coal to oils, motor fuels, and chemical feedstocks was available in Germany on industrial scale. The first hydrogenation plant was commissioned in Leuna in 1927. This plant employed the sump-phase and gas-phase hydrogenation processes developed by Bergius and Pier. At the same time the Pott Broche process for production of coal extracts and the Fischer-Tropsch synthesis for production of motor spirit and chemical feedstock were under development in Germany. After World War II, no attempt was made to reactivate the coal liquefaction technology, primarily because of economical reasons. Only since the oil crisis in 1973 further development was done on sump-phase hydrogenation for production of distillate oils from coal. The present activities are shown on table 1.

Compared to the earlier German hydrogenation process the new developments are featured particularly by the following conditions:

- Removal of solids and residual oils from the hydrogenation process by distillation rather than by mechanical separation.
- Recycling of only distillate oil for coal slurry preparation which means reduction of asphaltene concentration in the hydrogenation reaction.
- Use of the distillation residue for production of hydrogen in a downstream gasification plant.

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COMPANY	SITE (DISTRICT)	CAPACITY (COAL T/D)	BUDGET MM \$	SPONSOR	TIME SCHEDULE											
					74 75 76 77 78 79 80 81 82 83 84											
Bergbau- Forschung	Essen (Ruhr)	.5	16	State Gvt. NW (MWMV)	plant running											
Ruhrkohle Veba Oel	Bohrup (Ruhr)	200	150													
Saarberg	Reden (Saar)	.5	4	Federal Gvt. (BMFT) and State Gvt. Saar												
	Völklingen (Saar)	6	28													
Rheinbraun	Wesseling (Rhein)	.25	3	Federal Gvt. (BMFT)												

Tab. 1: Current coal hydrogenation projects in Germany

By these modifications the following improvements can be achieved:

- Lowering of the process pressure down to 300 bar
- Increase of the specific reactor throughput
- Minimize the residue problems by only producing an easily disposable mineral slag.
- Substantially increase thermal efficiency and, thus, process economics.

The Experimental Plant

In an experimental plant of Bergbau-Forschung, Essen, work is done since 1976 on the modified hydrogenation process. Work meanwhile exceeds 100 test runs totalling more than 20 000 hours of operation under hydrogenation conditions. Typical run conditions for a German bituminous coal are shown on table 2.

EXPERIMENTAL PLANT OPERATION

Reactor temperature	°C	475
Preheater outlet temp.	°C	420
Make-up hydrogen	m ³ /kg maf coal	1.00
H ₂ -Partial pressure at preheater inlet	bar	250
Total pressure	bar	300
Coal throughput	kg/l hr	.5 to .75
Type of recycle oil	middle a. heavy distillate	
Solids concn. in slurry	%	> 40
Coal particle size	mm	< .1

Tab. 2: Typical run conditions for a German coal.

Fig. 1 shows a simplified flow scheme of the experimental plant.

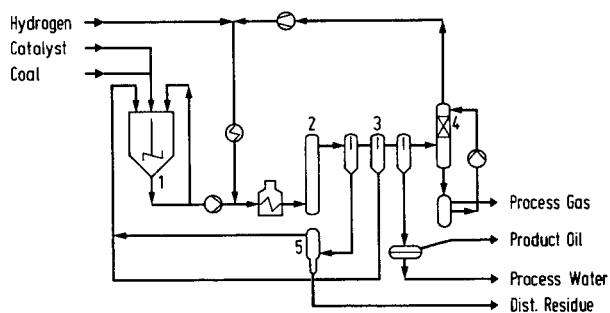


Fig. 1: BERGBAU-FORSCHUNG EXPERIMENTAL PLANT
 1 Slurry Preparation 2 Conversion 3 Separation
 4 Recycle Gas Scrubbing 5 Vacuum Flash

A pumpable slurry is made up by ground coal, recycled distillate oil, and catalyst. The slurry is fed to the hydrogenation reactor via a pre-heater. Upstream the pre-heater high-pressure hydrogen is added. After leaving the reactor the hydrogenation products are led to a series of three high-pressure separators. From the first vessel high- and non-boiling oils are drawn off together with all the solids viz some unconverted coal, mineral matter, and catalyst. The liquid is treated in a vacuum flash unit to yield a distillate oil containing no solids. Mostly middle oil is obtained from the second separator and also used for slurry preparation. In the third separator the net product oil is recovered. It consists of only light oil and middle oil. The gases that also form under reaction conditions are for the most part hydrocarbons. They are removed from the recycle gas by high-pressure oil scrubbing.

All the oils and gases produced in the hydrogenation step need upgrading to give saleable products.

Typical oil yield C₅+ from German bituminous coal is around 50 % w/w, as was shown in BF experimental-plant runs under conditions listed in table 2.

Product Oil

The distillate oil accounts for the largest portion of the product slate, i.e. for 50 % relative to the maf feed coal. The boiling point of the product oil, on average, ranges between 50 and 320°C, 30 % of the oil being in the boiling range below 200°C. Oil boiling above 320°C is not produced as net product with the new German coal hydrogenation process. It is all recycled and therefore out of the net balance.

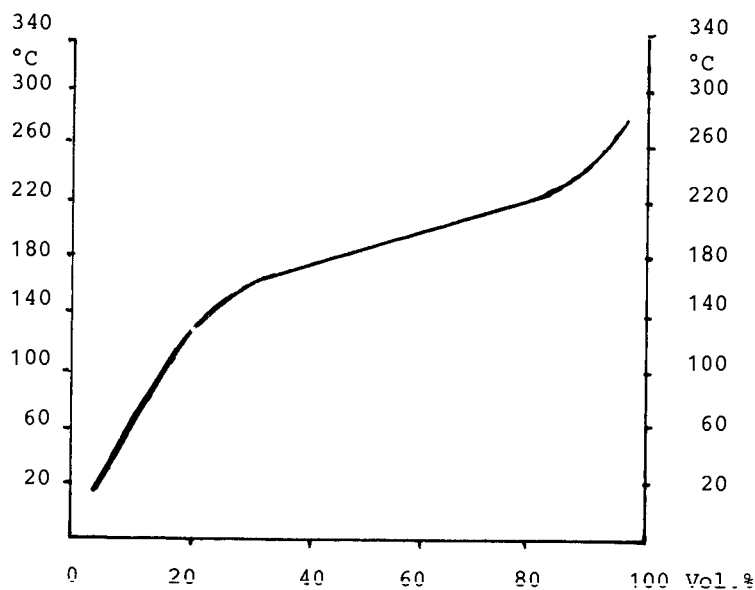
So far no detailed breakdown of all the components contained in the coal oil can be given. Sure we do know roughly the oil composition in terms of group type analyses, and there is no doubt on what individual structures the mixture is basically composed of.

However because of its origin the oil contains countless isomer compounds not only with regard to the carbon skeletons but also to the different partially hydrogenated aromatics. The product slate is further complicated due to the presence of phenol and its homologous compounds and to the presence of various nitrogen containing compounds. So only few individual compounds as phenol, all of the cresols, toluene, naphthalene, and tetrahydronaphthalene account for more than 1 % of the total oil quantity. A lot of compounds, however,

account for less than 0.1 per cent.
Some data on the properties and analytical composition of the light and medium boiling oil fraction, respectively, is listed below.

		Light Oil	Middle Oil
boiling range	°C	C ₅ - 200	200 ~ 325
density/15°C	g cm ⁻³	0.865	0.990
heating value	kJ kg ⁻¹	41 000	38 500
elemental analysis			
C	p.ct.,w/w	85.3	87.4
H	"	11.1	9.1
O	"	3.5	3.0
N	"	0.24	0.60
S	"	0.1	0.1
group type analysis			
neutral oil	p.ct.,w/w	84.35	77.3
phenols		15.4	16.2
bases		0.25	6.5

Figure 2 shows the boiling diagram of a typical product oil.



Residue

In the new German process all the remaining solids from the liquefaction step are kept in the flash distillation residue as is done also in some U.S. processes. In addition to the solids the residue contains the so-called asphaltoles, asphaltenes, as well as some heavy oil.

At elevated temperatures the organic matter forms a melt that keeps the solids suspended. Thus the residue represents a pumpable liquid that may easily be transferred to a pressurized gasifier. There by partial oxidation the hydrogen required for the liquefaction stage can be produced. Residue gasification is part of the overall process design but so far has not been investigated experimentally.

Approximately 25 p.ct. of the organic matter of the feed coal is bound in the flash distillation residue. The table gives information on the average analysis of such a residue.

Flash Distillation Residue Analysis

softening point	°C	180
volatile matter	p.ct.,w/w	30
ash content	"	26
pyridine insolubles	"	52
asphaltoles	"	9
asphaltenes	"	21
heavy oil	"	18

Hydrocarbon Gases

In bituminous coal hydrogenation gas formation mainly consists of hydrocarbons. In the plant there are several different process gases having different composition. The question whether these streams either should be combined or treated separately can only be discussed in commercial scale design. In the experimental plant the different streams are only measured and analyzed. From the analytical results we compute the overall hydrocarbon gas production based on the feed coal. This information is listed in the following table:

Hydrocarbon Gases

		saturates	olefins
methane	p.ct. w/w maf. coal	6.8	
ethane	"	5.7	
ethene	"		0.1
propane	"	5.6	
propene	"		0.3
n-butane	"	2.8	
i-butane	"	0.7	
butenes	"		0.2
total		21.6	0.6
		22.2	

In coal liquefaction the hydrocarbon gases are regarded as unavailable by-products. Nonetheless, at least the C₂ through C₄ hydrocarbons can be commercialized as valuable chemical feedstocks or fuel gases.

Water and Inorganic Gases

The inorganic compounds water, hydrogen sulfide, and ammonia as well as carbon monoxide and carbon dioxide are basically formed as by-products of coal hydrogenation. The quantities produced depend on the heteroatoms content (oxygen, nitrogen, sulfur) of the feed coal. These heteroatoms are partly converted to form hydrogen compounds.

The oxygen contained in coal is partly removed during hydrogenation as carbon monoxide and dioxide, the monoxide presumably being formed from dioxide by reduction with hydrogen. The carbon dioxide originates via decarboxylation from carboxylic groups present in the coal.

The denitrification and desulfurization reactions taking place along with the degradation of the coal is to be considered an advantage. While upgrading coal oil the heteroatoms left have to be removed anyway. On the other hand, the formation of some water from oxygen in coal may be taken as a drawback because of the consumption of hydrogen and the removal of potentially valuable phenols.

The product water is let down from high pressure together with the net product oil, and the two layers formed are subsequently separated. Dissolved in the water there are some phenols and inorganic compounds. Carbon monoxide has only poor solubility in the liquids

so it has to be removed from the high pressure gas by continuous release of some recycle gas. Carbon dioxide, ammonia, and hydrogen sulfide however dissolve sufficiently in water to be easily scrubbed from the high pressure gas by injecting some additional water. Consequently inorganic salts such as ammonium carbonate and sulfides are also present. Refining the process waste water will accordingly need much effort in commercial scale liquefaction.

Hydrogen Consumption

Hydrogen consumption on maf feed coal is 6.5 to 7.5 per cent computed on the maf feed coal, as measured in the BF experiments under the conditions listed in table 2. The consumption values cover both the chemically reacted hydrogen and the unavoidable losses. These have been determined to be about 15 % on the total hydrogen consumption. In result, the hydrogen consumed in reaction amounts to 5.5 to 6.5 per cent on maf coal.

When reducing hydrogenation severity and thus the yields - only 40 % instead of 50 % for oil, and 13 % instead of 23 % for gas - correspondingly the chemical hydrogen consumption is reduced to 4 %.

Because of the many different ways the hydrogen reacts with coal and the intermediate products, it is difficult to determine what amount of hydrogen is actually consumed with each of it. Methane for instance maybe formed from primary, secondary, and tertiary carbon atoms initially bound in coal. Each way implies a different hydrogen requirement.

Status of Development

The data and experiences from the BF experiments have been used to support design and engineering work on a 200 t/d pilot plant. The process flow sheet is essentially identical to the one of the experimental unit. Presently this demonstration project is under construction near Bottrop/Essen, Germany. The plant will be operational in mid - 1981. The program is under the responsibility of Ruhrkohle AG and Veba Oel AG, and the State Government of Northrhine-Westfalia gives major financial support.